CHARGE NUMBER: 2525

PROJECT TITLE: NATURAL PRODUCTS CHEMISTRY AND BOTANICAL INVESTIGATIONS

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I. ORGANIC CHEMISTRY

The development of new synthetic methods for the preparation of tobacco identical glycosides continues. Benzyl 4,6-di-O-acetyl-2-O-benzoyl-α-D-mannopyranoside was treated with α-D-mannose pentaacetate in methylene chloride and excess boron trifluoride etherate to give a 75% isolated yield of benzyl 4,6-di-O-acetyl-2-O-benzoyl-3-O(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside. This experiment demonstrates the utility of the boron-trifluoride etherate mediated glycosidation reaction in the synthesis of disaccharides. This method is an improvement over classical methods which require the tetra-O-acetylmannosyl bromide and heavy metal salts.

Additional quantities of phenethyl β-D-glucopyranoside and guiacyl β-D-glucopyranoside have been prepared for smoke studies and subjective testing.[1]

Synthesis of additional quantities of the cigarette beetle pheromone (± serricornin) continues.[2] Approximately 14g of pheromone was supplied to Project 1101 for additional field testing experiments.

Work continues on the synthesis and characterization of sclaral ether flavorants. This class of flavor compounds, generally described as "woody" character materials, shows much promise as tobacco flavorants. An invention record, with appropriate chemical and subjective characterizations, has been prepared for filing with the Patent Office.[3]

The preparation of a specifically labeled menthol glycoside has been completed.[4] The preparation involved reaction of (1,3-^{14}C-propyl)-menthol with acetobromoglucose, followed by deacetylation with sodium methoxide in methanol. The yield of (1,3-^{14}C-propyl)-menthol β-D-glucose was 3.7 μCi.

II. NATURAL PRODUCTS CHEMISTRY

Work continues on the preparation and characterization of radiolabeled tobacco identical hydrocarbons.[5] As part of a program to investigate the smoke chemistry of this class of compounds, separations methodology is currently under development. At ambient temperature adequate resolution and peak shape was obtained in the HPLC analysis for alkanes smaller than n-C_{32}. The effect of raising the column temperature on resolution and peak shape is being investigated. The column temperature tested was from 31° to 50°C using an Altex Ultrasphere ODS column on a Rainer LC column heater. Alkanes tested

included n-C_{20} thru n-C_{40}. A small loss in resolution and a significant improvement in peak shape was observed as the temperature was increased. The improvement in the peak shape was sufficient to allow for the detection of 1-5 μg quantities of n-C_{30} and n-C_{40} using the FID detector.

Efforts continue in a cooperative tobacco breeding study with Dr. E. Wernsman at NCSU (North Carolina State University).[7] Green leaf disks (2.5 cm) from approximately the sixth leaf of each plant in burley families originating from crosses of (Galpao Coumn x Greenville 115) S1 x Kentucky 14, suspected to be segregating for abienol synthesis capability, were collected and analyzed for cis abienol. As the plants flowered they were topped, but not suckered. Upon completion of leaf disk abienol analyses[6] (approximately 3.5 weeks after topping) pollinations were made on specific plants of interest in each family, while remaining plants, both abienol producers and non-producers, were closely hand suckered. Families of plants were stalk cut, speared, and hung in a highly ventilated curing shed. This was 21 days after plants had been suckered and last sidedressed, and six weeks following topping.

Following the completion of curing, leaves from all abienol synthesizing plants were stripped, separated into two stalk positions (midstalk and tips), and leaves from multiple plants in each family composited. The leaves were tied and tagged to identify their family, abienol content, and stalk position, and stored in plastic bags. Leaf from plants in low abienol content were handled in a similar manner.

Observations of plants during the yellowing phase of curing revealed unique characteristics of these tobaccos compared to traditional burley. Complete chlorophyll degradation in traditional burley results in a pale yellow leaf. These tobaccos posess a rich orange color at the end of yellowing. In stripping the leaf, it was noted that the tobaccos were exceedingly sticky, and that the exudate accumulating on the worker's hands imparted a very strong, sweet, fruity, and pleasant aroma. Leaf midveins and plant stalks also possessed an unusually high quantity of what appears to be trichome exudate.

Leaf color varied with stalk position from buff tips, reddish-brown leaf, to red tips. Leaves possess very good order-holding capacity, an excellent finish, and are exceedingly elastic. The quantity of oil in the leaf is very high. Cursory glances of adaxial leaf surfaces suggest variegated areas of the lamina; in reality these were sections of oil extrusion due to compression. The leaf has a pleasant tobacco aroma, particularly the abienol producers, which is different from that of a typical burley tobacco.

Approximately 35 lbs. of cured leaf has been obtained from NCSU. These samples are currently being evaluated for leaf chemistry, physical properties, and subjective qualities.[8,9]

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III. REFERENCES

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